A FLEXIBLE AND EASY-TO-USE CONTAMINANT FATE/TRANSPORT MODEL FOR STREAMS

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Abstract

The Contaminant Model for Streams (CMS) was developed for studies where data and resources for model application are limited. CMS can be relatively easily and quickly applied, yet it is a versatile model that can be used for a variety of conditions ranging from short term spill modeling to multi-year simulations of contaminant fate in stream water and bottom sediments. CMS was developed to fill a gap in the Adaptive Risk Assessment Modeling System (ARAMS). Before the addition of CMS, ARAMS did not have a one-dimensional, contaminant transport and fate model for streams that could simulate water column and sediment bed interactions.

CMS was developed such that it can be applied within the ARAMS framework and also can be run as a stand-alone application outside of ARAMS. The model can be used to simulate a wide range of conditions from spill simulations with time steps in seconds to long-term simulations with time steps of about a year. It can be applied for both organic and inorganic contaminants, and the available fate and transport processes include advection and diffusion along the stream reach, settling, resuspension, burial, volatilization, decay or degradation, and diffusion between the water column and the sediment pore water. Suspended solids can be transported, or a steady-state concentration may be input. The ARAMS version does not presently include solids transport, and steady-state, uniform hydraulic conditions are assumed within the modeled reach. Time-varying upstream loadings and flows can be applied, but flows are updated instantaneously throughout the reach, i.e., there is no hydraulic routing feature, which reduces model complexity.

The model user interface provides an easy-to-use method for quickly setting up the model and examining results. The interface also allows the user to select the methods and parameters used for the numerical solutions. The solution methods were selected to result in very short computer execution time for most applications. The model was verified against analytical solutions and results from two other models developed by ERDC, RECOVERY and PREWet, the latter of which uses an analytical solution method. This report describes the model and its verification.

INTRODUCTION

Background

Although there are many water quality models for streams, there was not a versatile, yet easy-to-use, model for contaminant transport and fate in streams prior to the development of the Contaminant Model for Streams (CMS). Such a model was needed for studies involving health risk assessment, which are often characterized by limited data and time to produce results. An easy-to-use, yet flexible model was needed for predicting short- and long-term concentrations of contaminants in the water column and bottom sediments.

The Adaptive Risk Assessment Modeling System (ARAMS) was developed for the Army by ERDC and the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) to provide a reliable platform for conducting human and ecological health risk assessment. ARAMS integrates multimedia fate/transport and multipathway exposure and uptake with effects assessment to characterize risk. Although several models are available in ARAMS for fate/transport in water, there was not a model for predicting fate of contaminants in streams with sediment interactions. There are many other riverine water quality models available that were considered for use in ARAMS, however, none of these models met the requirements without introducing excessive complexity.

Objectives

The overall objective of this study was to develop a flexible, but easy-to-use, one-dimensional (1D), numerical contaminant model for streams and rivers. Other objectives were:

- to be able to predict contaminant concentrations in the water column and sediment bed and include the effects of sediment processes and interactions;
- to be able to simulate short-term spill concentrations, as well as long term fate;

- to provide some degree of freedom over the numerical solution settings, but still be easy to setup and run and quickly provide useful results; and
- to provide a user interface to facilitate ease of use for model setup and quick viewing of results.

GOVERNING EQUATIONS

The fundamental law utilized in the development of the CMS is conservation of mass along the longitudinal axis (flow direction) of a surface water body, such as streams and rivers. The stream surface water is represented by a 1D (longitudinal) discretization for mass balance, where mass concentrations are assumed to be uniform across the width and depth of the stream. Constituent mass balance is performed for the water column and sediment bed. The bed is treated as a single active layer. The bed layer for each longitudinal segment is independent of other longitudinal bed segments, i.e., there is no longitudinal transport or transfer within the bed. Each bed layer interacts with only the water column immediately above the bed segment. Numerical solution schemes are used to provide flexibility for simulating variable inputs and a variety of processes.

There are 3 unknowns, contaminant concentration in the water column and in the bed and suspended solids concentration, if the solids transport option is chosen. For contaminants, the 2 unknowns require 2 equations, a mass balance equation for the water column and for the bed. For suspended solids, a mass balance equation for the water column is required. Each of these equations is presented along with any assumptions and supporting equations.

Water Column Contaminants

The dependent, state variable for contaminants in the water column is concentration of total chemical mass (dissolved and particulate) on a total water volume basis. The governing equation becomes,

$$\frac{\partial c_w}{\partial t} + U \frac{\partial c_w}{\partial x} = D_x \frac{\partial^2 c_w}{\partial x^2} - \left(k_{dw} + \frac{k_v}{H}\right) F_{dw} c_w - k_{pw} F_{pw} c_w - \frac{V_s}{H} F_{pw} c_w + \frac{V_r}{H} c_b - \frac{V_d}{H} \left(F_{dw} c_w - F_{db} c_b\right) \qquad (1)$$

where,

c_b = concentration of the constituent in the sediment bed (M/L³), total mass on a total volume basis

c_w = concentration of the constituent in the water column (M/L³), total mass on a total volume basis

D_x = longitudinal diffusion coefficient (L²/T)

F_{db} = fraction of the constituent dissolved in the sediment bed pore water

F_{dw} = fraction of the constituent dissolved in the water column

F_{pw} = fraction of the constituent in particulate form in the water column

H = hydraulic depth of the stream (L)

k_{dw} = decay rate of dissolved constituent in the water column (T⁻¹)

k_{pw} = decay rate of particulate constituent in the water column (T⁻¹)

k_v = volatilization rate of the constituent (L/T)

U = mean velocity (L/T)

V_d = mass transfer rate across the sediment-water interface resulting from diffusion of the dissolved constituent (L/T)

V_r = active sediment layer resuspension rate (L/T)

V_s = suspended solids settling rate (L/T)

x = downstream distance (L)

Equation 1 assumes reversible, equilibrium partitioning between sediment solids and water. In addition to the 1D assumption, uniform velocity and dispersion are assumed along the modeled stream reach.

The processes included in the water column mass balance for contaminants are advection, diffusion, settling of particulate mass, resuspension of sediment bed mass, dissolved mass transfer across the sediment-water interface, degradation/decay, and volatilization. The mass transfer across the sediment-water interface is actually a diffusive flow that is dependent upon the concentration gradient of the dissolved mass between the water column and the sediment bed. The volatilization rate is multiplied by the fraction dissolved in the water column because only this fraction is assumed to volatilize. The resuspension velocity is not multiplied by either the fraction dissolved or fraction particulate because both phases are assumed to be introduced into the water column during resuspension. However, settling only involves the particulate fraction that is in the water column. The terms for the fraction dissolved and fraction particulate in both the water column and sediment bed were derived using the water column and sediment bed distribution coefficients for reversible, linear, equilibrium partitioning between dissolved and sorbed phases.

Options are built into the model to either input the volatilization rate or to calculate it based upon Henry's Law and Whitman's two-film theory (Chapra 1997) as modified for the influence of water flow and wind. With the two-film theory, there is no volatilization in the absence of wind. However, this is not always the case for swift streams and highly volatile constituents. Therefore, a minimum value for the gas side mass transfer coefficient, K_g, of 100 m/day is set to prevent limiting the volatilization rate under these circumstances. This is also the approach used in both WASP (Wool et al. 2001) and ICM/TOXI (Wang et al. draft report) for fast-moving streams.

It is assumed that the mass transfer across the sediment-water interface acts in a similar manner to the two-film model for volatilization calculations. A two-layer model does not exist for diffusion between the sediment pore water and the water column, but the transfer rate can be calculated based on the properties on each side of the boundary and is limited by the lowest transfer velocity. To account for influences in the water column and the sediment bed, the mass transfer velocity is calculated using formulations derived by Schink and Guinasso (1977) and Di Toro (Di Toro et al., 1981), respectively. The lower of the two velocities, or the limiting rate, is then used in the water column and bed calculations.

The terms in Equation 1 can be grouped to form a simplified version of the advection/diffusion/reaction equation,

$$\frac{\partial c_w}{\partial t} = -U\frac{\partial c_w}{\partial x} + D_x\frac{\partial^2 c_w}{\partial x^2} - kc_w + q \tag{2}$$

where:

$$k = \left(k_{dw} + \frac{k_v}{H} + \frac{V_d}{H}\right)F_{dw} + \left(k_{pw} + \frac{V_s}{H}\right)F_{pw} \tag{3}$$

$$q = \frac{V_r}{H}c_b + \frac{V_d}{H}F_{db}c_b \tag{4}$$

The term k includes all of the loss terms for the constituent in the water column. Since the terms for resuspension and mass transfer from the sediment bed do not involve the water column concentration, they are grouped together and treated as a source term, q.

Bed Contaminants
The mass balance for total (dissolved and particulate) contaminant mass in the sediment bed for each stream segment is stated as

$$\frac{dc_b}{dt} = -\left(k_{db}F_{db} + k_{pb}F_{pb}\right)c_b + \frac{V_d}{h}\left(F_{dw}c_w - F_{db}c_b\right) - \frac{V_r}{h}c_b + \frac{V_s}{h}F_{pw}c_w - \frac{V_b}{h}c_b \tag{5}$$

where,

F_{pb} = fraction of the constituent in particulate form in the bed

h = active sediment layer thickness (L)

k_{db} = decay rate of dissolved constituent in bed pore water (T^{-1})

k_{pb} = decay rate of particulate constituent in the bed (T^{-1})

V_b = active sediment layer burial rate (L/T)

Equation 5 includes the following processes for the bed: decay or degradation, mass transfer of dissolved constituents across the sediment-water interface, resuspension to the water column, settling of particulate constituents from the water column, and burial to lower sediment layers. Longitudinal exchange between adjacent bed segments, such as pore water flow or diffusion along the stream flow axis, is assumed to be negligible.

Suspended Solids Transport

If suspended solids in the water column are transported, then they are treated similar to a contaminant constituent that does not decay or volatilize. The solids are advected and dispersed along the length of the stream reach in the same manner as the constituents but do not have all of the same loss mechanisms. The only loss mechanism for suspended solids in the water column is settling. In the same manner there is an influx of solids to the water column from any sediment resuspension that occurs. The suspended solids mass balance in the water column is stated as,

$$\frac{\partial S}{\partial t} + U \frac{\partial S}{\partial x} = D_x \frac{\partial^2 S}{\partial x^2} - \frac{V_s}{H} S + \frac{V_r}{H} S_b \tag{6}$$

where S is the concentration of solids in the water column (M/L^3), and S_b is the concentration of solids in the sediment bed (M/L^3), which is the same as the sediment bulk density, $\rho_b = (1-\phi)\rho_s$, where Φ is the porosity of the sediment bed and ρ_s is the dry sediment density (M/L^3). The remaining variables are the same as those defined previously.

The CMS can also be run with a steady-state solids concentration. In this case, solids will not be modeled in the water column, and the background solids concentration is specified and held constant for the entire simulation period. The state variable for solids is the total solids concentration, which includes both inorganic and organic solids.

A single active sediment layer is modeled. The active bed layer is assumed to have constant properties, thus, the thickness, volume, porosity, bulk density, and solids mass are constant over time (i.e., steady-state) and assumed to be uniform over the stream reach. Solids and contaminant mass that is buried to deep sediments is assumed to be lost. Performing a steady-state solids balance for the bed layer results in the following relationship,

$$V_b = \frac{V_s S}{S_b} - V_r \tag{7}$$

where all variables have been previously defined. With the settling and resuspension rates specified, the burial rate can be determined, which is required for the bed contaminant mass balance (Equation 5). Alternatively, any two of the three rates in Equation 11 could be specified and the unknown rate solved.

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STREAM SYSTEM DESCRIPTION

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The stream system is a single reach with uniform hydraulic conditions, but this may be expanded in a future version to allow multiple reaches with different hydraulic conditions for each. For the modeled reach, multiple points of interest for output can be defined through user-entered usage locations. A usage location is a point at a given downstream distance from the farthest upstream node and may indicate a withdrawal point, a habitat for a species of

interest, or any point where the constituent concentration is of interest. For each usage location specified by the user, an associated distance is required for the usage location. The total length of the stream reach that will be modeled is the distance to the farthest usage location. Time-varying flow and loading values for water, constituents, and solids can be specified at the upstream boundary along with the average background flow and concentrations.

Background Flow and Flux Data

Background flow rate, such as the mean annual flow rate, suspended solids concentration, and constituent concentrations can be specified for the reach being modeled. In addition to the constant, steady-state background flow and loadings, time-varying flows and loads can also be specified at the upstream boundary. Time-varying loading, or flux, data are entered for water, suspended solids, and all modeled contaminant constituents. These inputs may be specified at any time point after time zero, but values for all variables must be specified for time zero, except for suspended solids, which does not need to be entered if a steady-state solids balance is selected in the project settings. In this case, the background concentration is used as the steady-state concentration for the entire stream reach. The background and time-varying fluxes are added together to set the upstream boundary conditions.

Hydraulic Conditions

The hydraulic conditions are not solved, but are specified. Flow conditions are assumed to be steady-state within each loading update interval and uniform over the modeled reach. Flows can change for each loading update interval due to changes in the loading flow rate, but flow rate, depth and flow area are assumed to change instantaneously over the entire reach, thus, there is no hydraulic or hydrologic routing and no transient flow features. Three options are provided for specifying hydraulic conditions:
1. specify stream width and depth as constants throughout the reach;
2. specify stream cross-sectional area and depth as a constant throughout the reach; and
3. calculate the stream cross-sectional area of flow and hydraulic depth as a function of flow in the reach.

Boundary Conditions

Dirichlet boundary conditions are used for the upstream boundary, thus, allowing the user to specify concentrations or loading flux at the upstream boundary (Chapra 1997). The upstream boundary also uses a pipe condition where advective flow is allowed into the first segment, but diffusion is not allowed across the boundary so that mass will not move backward out of the system. The concentration entering the reach is determined using the flow weighted mass balance of the background and loading. The boundary condition at the end of the reach is an open boundary where both advection and diffusion are allowed across the boundary. A Neumann condition is used to specify the derivative of the concentration at the downstream boundary (Chapra 1997). The concentration gradient with respect to downstream distance across the boundary at the last segment is assumed to be zero. Therefore, the downstream boundary concentration is equal to the concentration of the last segment.

The user may specify an upstream boundary concentration or flux at any time update interval. For time steps where a boundary value is not updated, the model will perform a linear interpolation between the previous and next boundary update to determine the value that should be used for each model time step. A boundary condition must be specified for time zero and, if no other concentrations are specified, that value will be used as a steady-state condition for every time step.

SOLUTION METHODS

An implicit, finite difference, numerical solution scheme is used to solve the partial differential equations for surface water contaminant and suspended sediment concentrations (Equations 1 and 6). A choice between two numerical integration schemes is provided to solve the ordinary differential equation for sediment bed contaminant mass (Equation 5).

A variation of the Crank-Nicolson (CR) method (Chapra 1997) was selected for the implicit, finite difference scheme. The CR scheme is a centered in time and centered in space approximation. This method is second-order accurate and is stable even for large time steps. The CR scheme reduces numerical dissipation by approximating the spatial derivatives at both the present and future time steps. These estimates are then averaged to obtain a spatial estimate that corresponds to the midpoint of the time step. The time weighting in the modified CR method is performed using a coefficient of implicity (θ) that is specified by the user rather than a value of 0.5 that is used for the general form of the CR method. If θ is set to a value of *0.0*, the equation becomes fully explicit, and the only

values included are from the current time step. If a value of *1.0* is used, the equation is fully implicit and only values from the future time step are included. Upwind differencing for the advection term was added as an additional option. The main drawback to using the upwind differencing scheme is that it tends to introduce numerical diffusion into the solution, especially at high stream velocities or large spatial steps. However, this scheme introduces less artificial oscillation for sharp gradients than the central difference scheme and was added to the model to allow the user more flexibility and choices in solving a wider range of problems.

The option of using the Euler method or the fourth order Runge-Kutta method is provided for solving for the contaminant concentration in the sediment bed (i.e., Equation 5). The Euler method is easy to implement, but it is only first order accurate in time. The fourth order Runge-Kutta method uses estimates of the slope at four points to calculate an improved average slope for the time interval (Chapra 1997). Although the implicit solution for the water column is unconditionally stable, the solution for the bed is not and can generate oscillating, unrealistic concentrations for large time steps. An adaptive time stepping solution option has been implemented for solving the ordinary differential equation for the bed to ensure stable results.

MODEL VERIFICATION

Verification of the CMS has been performed using two different methods. First, the CMS was tested against an analytical solution for a contaminant spill in a stream. This test did not include sediment interactions or loss mechanisms, which also allowed for a test of conservation of mass in the water column as the contaminant moved along the stream reach. The CR scheme was used for the advection term, and a value of 0.5 was used for the coefficient of implicity for both the advection and diffusion terms. A 2kg mass of a conservative constituent was input during the first time step giving an initial concentration of 27.8 mg/L in the water column. Using a time step of 36 seconds, a spatial step of 20m, and a calculated velocity of 40800 m/day, the Courant number for this test was determined to be 0.85. The results showed that the numerical water column solution in the CMS perfectly conserved mass, and that the results matched the analytical solution very well as can be seen in Figure 1 for three different time points after the initial contamination of the stream.
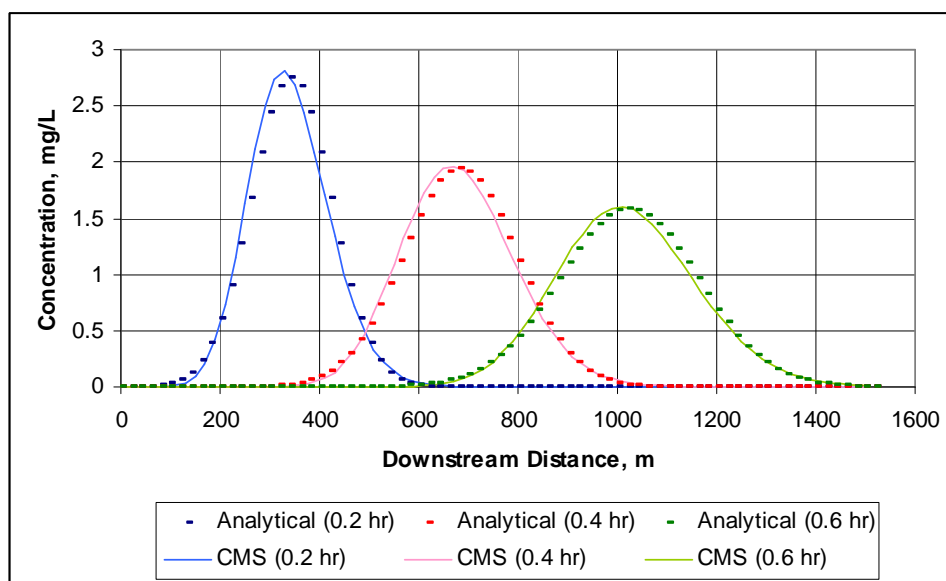
Figure 1 Comparison of CMS results with an analytical solution for a contaminant spill in a stream

Because there was no readily available, long-term constituent concentration data to validate the CMS, the second verification of the model equations was performed using two existing contaminant models: RECOVERY (Ruiz and Gerald 2001) and PREWet (Dortch and Gerald 1995). RECOVERY is a numerical, time varying model of water column and bed contaminant mass where the water column is a single, fully mixed compartment, and the bed is modeled with multiple layers over the depth. PREWet is a 1D (longitudinal), steady-state model with an analytical

solution. RECOVERY assumes a steady-state solids balance for the bed, and suspended solids are input and constant throughout the water column and over time.

One organic and one inorganic constituent were chosen for the model verification tests, and two test sets were run. The first test was a long-term, steady-state loading simulation run for 200 years, long enough for constituent concentrations in both the water column and sediment bed to reach steady-state values. All three models were compared for this test. The second test was a time-varying test case with stepped constituent influx concentrations over a simulation period of 100 years. The constituent flux was increased at 25 and 50 years and then decreased at 75 years. In this simulation, the constituent concentrations in the sediment bed were never allowed to reach steady-state. Only RECOVERY was run for CMS comparisons for this test because PREWet is a steady-state model.

The results of the steady-state test case are shown in Table 1 for an inflow concentration of 30 mg/L for both DDT and Chromium III. The results for CMS and PREWet are reported at the end of the modeled reach. The superscripts for the CMS model indicate the solids transport option that was used; one (1) indicates a steady-state solids balance, and two (2) indicates that the solids transport option was used.

Table 1 Steady-State Test Results

Model	Contaminant	Water Conc. (mg/L)	Sediment Conc. (mg/kg)
PREWet	DDT	26.97	168600
	Chromium III	27.34	171400
RECOVERY	DDT	26.6	166000
	Chromium III	27.4	171000
CMS[1]	DDT	27.0	168000
	Chromium III	27.3	171000
	Solids	150	
CMS[2]	DDT	26.8	184000
	Chromium III	27.2	187000
	Solids	135	
[1] steady-state solids balance option			
[2] solids transport option			

The results from all three models match well for the water column concentrations for both constituents. This is true for both the steady-state solids balance and with suspended solids transport. However, both the DDT and Chromium III sediment concentrations predicted by the CMS with solids transport are about 9.5% higher than all other predictions. The reasons for the difference is due to a gradient in the suspended solids concentration created along the stream reach, dropping from the inflow concentration of 150 mg/L at the upstream boundary to 135 mg/L at the end of the reach. The calculated resuspension velocities for each cell also decreased along the stream reach, and more constituent mass was bound in the bed at the low end of the reach. The RECOVERY and PREWet models used a steady solids concentration of 150 mg/L throughout.

A test was next performed using both the RECOVERY and PREWet models with the suspended solids concentration of 135 mg/L calculated by the CMS for the end of the stream reach. The results from this test are shown in Table 2 and verify that both the RECOVERY and PREWet models gave sediment concentrations closely matching the CMS when the calculated solids concentration from the CMS was used as the steady-state concentration for these models. This test helped to verify that the CMS is working properly, at least for a steady-state loading.

Table 2 Steady-state solutions for RECOVERY and PREWet using
modified suspended solids concentration of 135 mg/L

Model	Contaminant	Water Conc. (mg/L)	Sediment Conc. (mg/kg)
PREWet	DDT	26.68	184000
	Chromium III	27.08	187400
RECOVERY	DDT	26.4	181200

	Chromium III	27.2	186900

The second test case was run for the RECOVERY model and the CMS using the same data as the steady-state case above and stepping the constituent influx at 25-year intervals for each constituent. Table 4 shows the final results for both models at the end of the simulation and at the downstream end of the reach. The CMS run was made using the suspended solids transport routing option.

Table 3 Final results for RECOVERY and CMS models for the step function test case

Model	Contaminant	Water Conc. (mg/L)	Sediment Conc. (mg/kg)
RECOVERY[1]	DDT	13.36	86,621
	Chromium III	13.77	89,298
RECOVERY[2]	DDT	13.23	95,864
	Chromium III	13.65	98,915
CMS	DDT	13.4	97,400
	Chromium III	13.6	99,100
	Suspended Solids	135	
[1] steady-state concentration of 150 mg/L			
[2] steady-state concentration of 135 mg/L			

The superscripts for the RECOVERY model in Table 3 indicate the steady-state solids concentration that was used; one (1) indicates a steady-state concentration of 150 mg/L, and two (2) indicates a steady-state concentration of 135 mg/L corresponding to the value calculated by the CMS at the end of the reach. The comparison of CMS and RECOVERY results shows that the water concentrations are close. The sediment concentrations also agree fairly closely when the same suspended solids concentrations are used in the two models. The minor differences between the two results could be due to the fact that RECOVERY treats the entire reach as a single, fully mixed cell of homogeneous concentration, whereas, CMS computes a gradient in concentration along the reach. Differences may also arise from the fact that RECOVERY models multiple bed layers, whereas, CMS models only a single bed layer. This test verified the CMS for time-varying input data.

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